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Thermogravimetry of heteroleptic zinc tri-*tert*-butoxysilanethiolates: synthesis and crystal structure of bis(tri-*tert*-butoxysilanethiolato)(pyridine) zinc(II)

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Abstract

Thermal behaviour of three silanethiolate zinc complexes i.e., bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II), bis(tri-*tert*-butoxysilanethiolato)bis(*N*-methylimidazole) zinc(II) and bis(tri-*tert*-butoxysilanethiolato) (2-methylpyridine) zinc(II) was studied. In order to determine the steps involved in thermal decay, decomposition intermediates were identified by means of IR spectroscopy and solid residues were analysed. Enthalpies of undergoing processes were estimated on the basis of DTA curves. The results of the study were applied to the synthesis of a new complex – bis(tri-*tert*-butoxysilanethiolato)(pyridine) zinc(II). NMR and IR spectra of this complex were measured and crystal and molecular structures were determined.

Keywords: Zinc thiolates; Thermal analysis; Crystal structure

1. Introduction

Zinc complexes play an important role in biological chemistry. Almost 200 three-dimensional structures of zinc-containing proteins were described [1]. Four types of zinc binding sites were recognized with regard to zinc function, type of ligands and coordination geometries. These are catalytic, cocatalytic, structural sites and protein interface. Zinc-containing biochemical sites have been reviewed [1]. A catalytic zinc generally forms complexes with nitrogen, oxygen and sulphur donors of His, Glu, Asp and Cys aminoacid residues. It is not suprising than, that heteroleptic zinc thiolates with oxygen and nitrogen ligands have arisen interest of several scientific groups and the literature concerning the subject is ubiquitous. We recall here only some recent works, in which the reader may find more Ref. [2–6]. For a few years, we have also been engaged in a synthesis of silanethiolate complexes of zinc and cobalt mimicking active enzymatic site. The coordination number for such site is usually four or five and the geometry is distorted tetrahedral or trigonal bipyramidal [1]. We tried to restore the enzymatic environment of zinc in alcohol dehydrogenase using tri-*tert*-butoxysilanethiol. We were at least partly successful since we were able to synthesise the first zinc complexes with $ZnNO_2S_2$ core i.e., bis(tri-*tert*-butoxysilanethiolato) (acetonitrile) zinc(II) [7], bis(tri-*tert*-butoxysilanethiolato) (*N*-methylimidazole) zinc(II) and analogous complexes with 2-methylpyridine and 2,4-dimethylpyridine [8]. We prepared at least 20 thiolate zinc complexes and several isomorphous cobalt complexes—the syntheses and structures of most of them were published [7–12].

As catalytic function of zinc often requires change of ligand environment i.e., number of ligands and geometry of the complex, we would like to see whether such change is possible in case of our complexes. We chose bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II), bis(tri-*tert*-butoxysilanethiolato)bis(*N*-methylimidazole) zinc(II), bis(tri-*tert*-butoxysilanethiolato) (2-methylpyridine) zinc(II) and tried to introduce changes in the structure of these

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complexes by elevated temperature. Partial lost of heterocycle by heteroleptic thiolate zinc complex accompanied by structural changes was described by Bochmann et al. [13] for $Zn(2,4,6\text{-}^tBu_3C_6H_2)_2$(*N*-methylimidazole)$_2$ in hot toluene. We have not observed this in the case of our compounds, which were recrystallized from various solvents without changes, but it could be different situation when heating the complexes alone. Our second aim was to study the relative stability of the complexes and to see whether it is possible to compare the energy of Zn–N bonds formed by various heterocycles in our complexes on the basis of thermochemical data.

2. Experimental

2.1. Synthesis of complexes

The synthesis of bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**), bis(tri-*tert*-butoxysilanethiolato)-bis(*N*-methylimidazole) zinc(II) (**2**) and bis(tri-*tert*-butoxysilanethiolato)(2-methylpyridine) zinc(II) (**3**) was described in detail in our previous paper [8].

Bis(tri-*tert*-butoxysilanethiolato)(pyridine) zinc(II) (**4**) was prepared by heating 100 mg of **1** at 100 °C. When after approximately 3 h of heating 10% loss of weight was observed, the solid residue was recrystallized from acetonitrile. Colourless crystals of product were harvested, mp 169–171 °C. NMR data for **4** ($CDCl_3$), ^1H NMR, σ (ppm): 1.3254H(s) silanethiol Bu^t, 7.48–7.552H(m) pyridine *m*-CH, 7.88–7.971H(m) pyridine *p*-CH, 9.14–9.182H(m) pyridine *o*-CH. Elemental analysis for **4** Calc. for $C_{29}H_{59}NO_6S_2Si_2Zn$: C 49.51%; H 8.45%; N 1.99%; S 9.12%. Found: C 49.80%; H 8.47%; N 2.05%; S 8.99%.

2.2. Thermal analysis

The measurements were performed using a Q-1500 D derivatograph in a static air atmosphere, with α-Al_2O_3 as the reference compound, at a heating rate of 5 K/min. In a ceramic crucible, 200 mg samples were contained. The measurements were repeated in nitrogen atmosphere for compounds **1** and **3**.

2.3. Thermal analysis coupled with IR

The measurements were performed in a flow of argon using Netzsch thermobalance TG 209 coupled with Bruker IFS66 FTIR spectrometer. Approximately, 10 mg samples were contained in an aluminium crucible. The volatiles evolving from the heated sample were transported to the spectrometer chamber via thermostated pipe in the stream of argon.

2.4. Spectral measurements

IR spectra of tri-*tert*-butoxysilanethiol, *N*-methylimidazole and pyridine as films on KBr discs were recorded on Bruker IFS66 FTIR spectrometer. IR spectra of solid residues in KBr pellets were recorded on Mattson Genesis II Gold FTIR spectrometer. ^1H NMR spectrum was measured on Gemini 200 (200 MHz) spectrometer (TMS int.).

2.5. Analysis of the solid residue

Sulphur was determined using iodimetry, silicon was determined as silica by gravimetric analysis and zinc was determined complexometrically.

2.6. Structure determinations

Diffraction data were recorded on a KUMA KM4 diffractometer with graphite-monochromated Mo Kα radiation, equipped with Sapphire 2 CCD camera (Oxford Diffraction). Numerical absorption corrections were applied. The structure was solved with direct methods and refined with the SHELX97 program package [14,15] with the full-matrix least-squares refinement based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in geometrically idealized positions with isotropic temperature factors 1.2 times the equivalent isotropic temperature factors U_{eq} of their attached atoms. Crystal data, description of the diffraction experiment and details of structure refinement are presented in Table 1.

3. Results and discussion

3.1. Thermogravimetric (TG) and TG–IR studies

3.1.1. Bis(tri-tert-butoxysilanethiolato)bis(pyridine) zinc(II) (1)

TG, DTG and DTA curves obtained for complex **1** are shown in Fig. 1. The compound decomposed in two consecutive steps. Decomposition began above 80 °C with the elimination of approximately 0.5 mol of pyridine per 1 mol of **1** (weight loss calculated 5.05%/found, average 4.4% tc). In the second step, represented by the sharp slope on the TG curve, entire decomposition of complex took place.

Second step underwent in the temperature range 170–270 °C. Both steps were endothermic. The final decomposition product consisted probably from zinc sulphide and zinc silicate. The content of zinc, sulphides and silica was determined in the residue as 23.5, 13 and 6%, respectively. We compared IR spectrum of the residue with the IR spectrum of zinc orthosilicate [16] and found the spectra to be virtually the same in the studied region, with the broad band of Si–O bond at 1080 cm^{-1}. Unfortunately, we are not able to suggest any formula fully consistent with the obtained results.

The thermal measurements for complex **1** were repeated on thermobalance coupled with IR spectrometer, so that the IR spectra of the released volatiles could be measured. TG–IR measurements were performed in argon atmosphere. Obtained TG and DTG curves are presented in

Table 1
Crystal data and structure refinement parameters for bis(tri-*tert*-butoxysilanethiolato)(pyridine) zinc(II) (**4**)

Identification code	**4**
Empirical formula	$C_{29}H_{59}NO_6S_2Si_2Zn$
Formula weight	703.44
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a	8.5900(3) Å
b	25.2430(9) Å
c	18.4510(8) Å
β	95.120(3)°
Volume	3984.9(3) $Å^3$
Z	4
Calculated density	1.173 Mg/m^3
Absorption coefficient	0.816 mm^{-1}
F(0 0 0)	1512
Crystal size	0.53 mm × 0.45 mm× 0.35 mm
Theta range for data collection	2.66–30.00 deg.
Limiting indices	$-12 \le h \le 12$, $-35 \le k \le 35$, $-25 \le l \le 25$
Reflections collected/unique	122687/11594
R (int)	0.0806
Completeness to $\theta = 30.00$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11594/8/430
Goodness-of-fit on F^2	1.191
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0718$
$wR2$	0.1284
R indices (all data)	$R1 = 0.0736$
$wR2$	0.1292
Largest diff. peak and hole	0.734 and −0.470 $eÅ^{-3}$

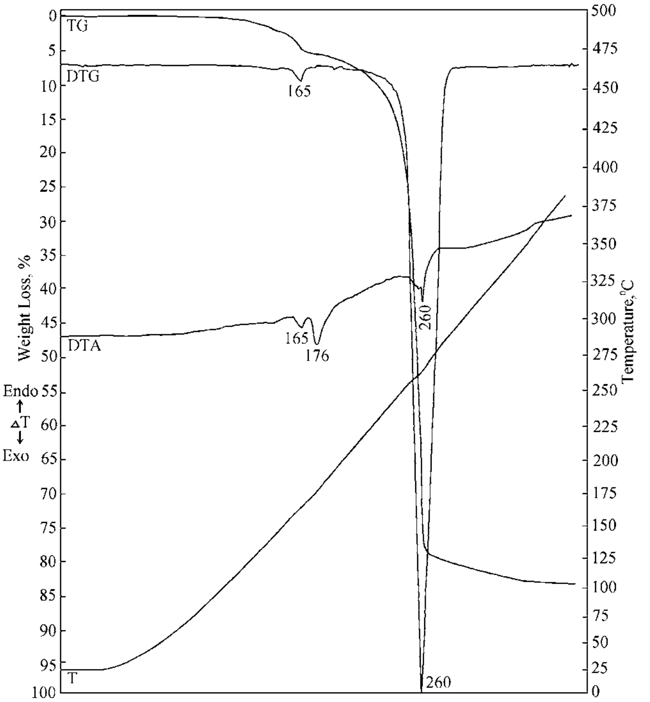


Fig. 1. TG, DTG and DTA curves for bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**) measured in the static air atmosphere.

Fig. 2. The temperature range and measured mass loss differed from the thermal analysis performed in the air atmosphere. Mass loss calculations indicated the release of one pyridine molecule from the complex in the first stage (weight loss calculated 10.11%/found 11%) in the temperature range 110–195 °C. The second stage connected with the release of the remainder of pyridine and most probably di-*tert*-butoxythiosilane underwent in the temperature range 196–260 °C.

IR spectra (Figs. 3–5) let to follow the decomposition processes in a more detailed manner. Up to 165 °C i.e., mass loss of 2.5% only the presence of pyridine could be found in IR spectra (Fig. 3). At higher temperatures, pyridine and di-*tert*-butoxythiosilane (or similar compound) evolved simultaneously (Figs. 4 and 5). The spectra of pyridine and tri-*tert*-butoxysilanethiol measured on the same apparatus are presented in Figs. 3 and 5 for comparison. We do not discuss the spectra in detail here, but we would like to draw reader's attention to bands of diagnostic value, which let to notice pyridine and *tert*-butoxysilyl group presence or absence in the volatiles. For pyridine, we have sought CH modes at 3063 and 3022 cm^{-1} (weak bands) and ring modes at 1604 cm^{-1} and for *tert*-butoxysilyl group CH modes at 2980 cm^{-1} (strong band) and SiOC modes at 1076 cm^{-1} (very strong band).

We assumed that the white, solid residue consisted of ZnO (weight percentage calculated 10.35%/ found 10.31%). Formation of ZnO is thermodynamically preferred to the formation of ZnS as enthalpy of formation for ZnO is almost twice the enthalpy of formation of ZnS ($\Delta H_{fZnO} = -83.24$ kcal/mol, $\Delta H_{fZnS} = -46.04$ kcal/mol [17]). It is also possible for **1** as tri-*tert*-butoxysilanethiol is chelating *O*,*S*-ligand. However, IR spectrum of the remaining solid revealed the presence of strong bands of Si–O in the

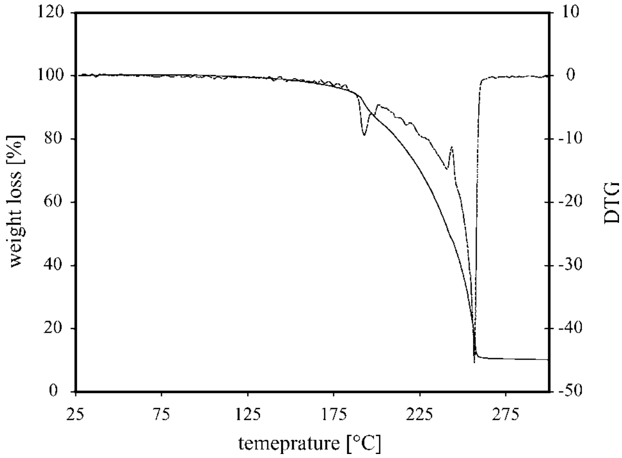


Fig. 2. TG and DTG curves for bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**) measured in the dynamic argon atmosphere.

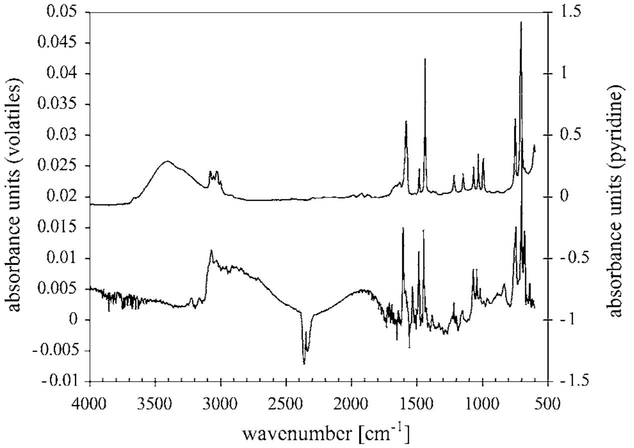


Fig. 3. IR spectrum of volatiles evolving during TG analysis of bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**) at 165 °C (lower spectrum) and IR spectrum of pyridine (upper spectrum).

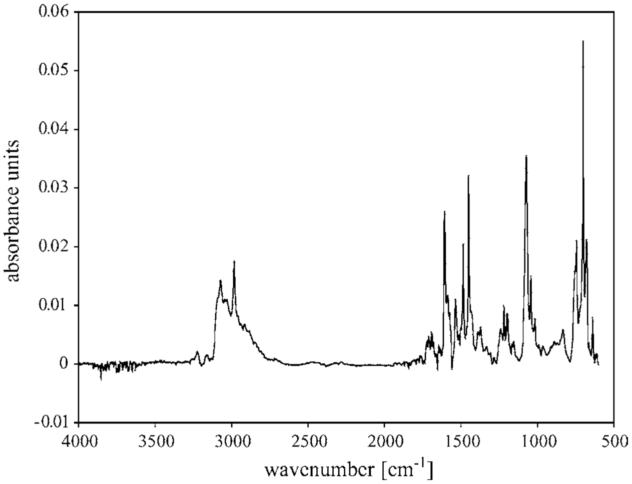


Fig. 4. IR spectrum of volatiles evolving during TG analysis of bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**) at 190 °C.

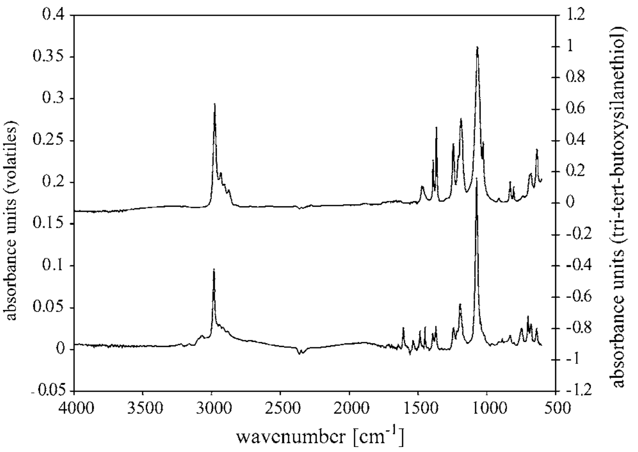


Fig. 5. IR spectrum of volatiles evolving during TG analysis of bis(tri-*tert*-butoxysilanethiolato)bis(pyridine) zinc(II) (**1**) at 275 °C (lower spectrum) and IR spectrum of tri-*tert*-butoxysilanethiol (upper spectrum).

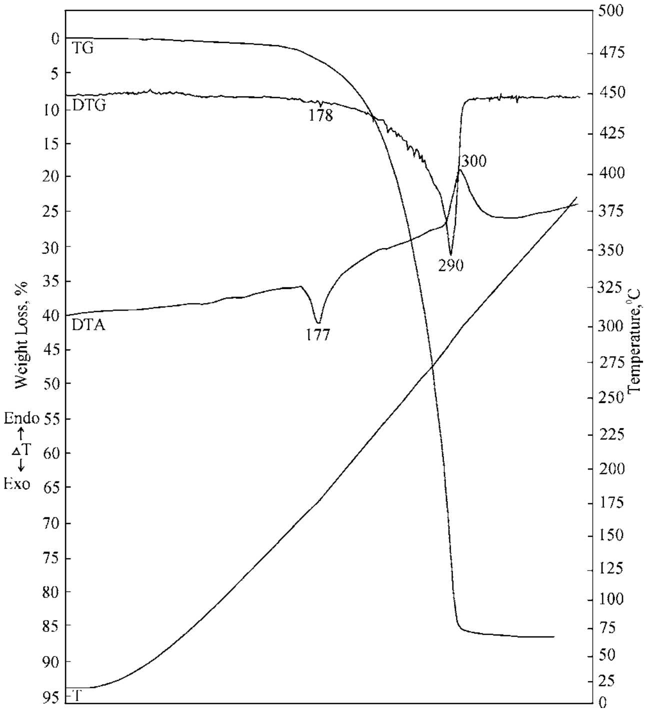


Fig. 6. TG, DTG and DTA curves for bis(tri-*tert*-butoxysilanethiolato)bis(*N*-methylimidazole) zinc(II) (**2**) measured in the static air atmosphere.

residue (1080 cm^{-1}) and finally, we are not able to suggest the nature of this product.

3.1.2. *Bis(tri-tert-butoxysilanethiolato)bis(N-methylimidazole) zinc(II) (**2**)*

The process of decomposition of bis(tri-*tert*-butoxysilanethiolato)bis(*N*-methylimidazole) zinc(II) (**2**) was similar to the process described above for **1** and underwent in two steps (Fig. 6). Slow process of release of *N*-methylimidazole began approximately at 90 °C and ended at 180 °C. The mass loss during this first step was less than 0.5 molecule of *N*-methylimidazole (weight loss calculated 5.2%/found 3.18%). This step was endothermic. The temperature range of the second step, connected with the simultaneous release of *N*-methylimidazole and tri-*tert*-butoxysilyl group was 180–300 °C and the process was exothermic. We assumed that this exothermic effect could be due to *N*-methylimidazole oxidation and therefore, we repeated the measurements in the nitrogen atmosphere (Fig. 7). Indeed in nitrogen atmosphere, we observed reversal of the effect; both steps were endothermic. The mass and analyses of solid residue indicated that the same product as in the case of **1** was formed. The thermal measurements for complex **2** were repeated on thermobalance coupled with IR, in argon atmosphere. The obtained TG and DTG curves and respective IR spectra, which can be obtained from the corresponding author on request, confirmed the decomposition pathway described above. The white solid residue formed in the argon atmosphere consisted probably of ZnO (?) (mass calculated 10.35%/ found 10.31%).

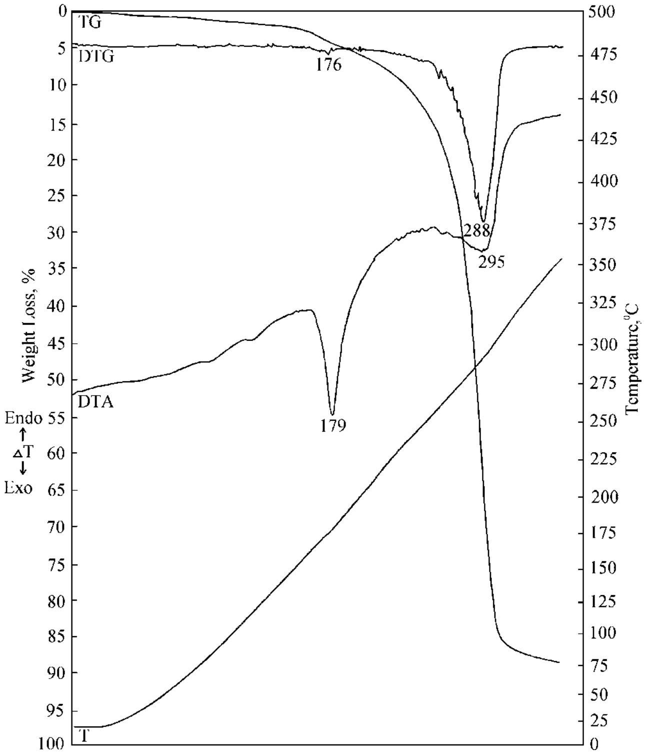


Fig. 7. TG, DTG and DTA curves for bis(tri-*tert*-butoxysilanethiolato)bis(*N*-methylimidazole) zinc(II) (**2**) measured in the static nitrogen atmosphere.

3.1.3. *Bis(tri-tert-butoxysilanethiolato) (2-methylpyridine) zinc(II) (**3**)*

Complex **3** also decomposed in two stages (Fig. 8). First step, not very distinct was probably connected with partial elimination of picoline and underwent at the temperature range 150–180 °C. The mass loss corresponded to the release of 0.25 molecule of picoline (weight loss calculated 3.2%/found 3%). Second step, which led to the final decomposition of the complex **3**, underwent between 175 and 250 °C. Both steps were endothermic (Fig. 8).

3.2. *Comparison of DTA curves for the studied compounds*

On the basis of DTA curves for **1**, **2** and **3**, which are presented in Figs. 1, 6 and 8, we estimated and compared the enthalpies of the first stage reactions for the three complexes. The enthalpies were calculated from the following formula: $\Delta H_1 = (A_s/A_r)\Delta H_r M$, where A_s area of DTA peak for the studied compound, A_r is area of DTA peak measured for the reference compound (benzoic acid) on the same apparatus, ΔH_r the enthalpy of melting of benzoic acid, which is 147.54 J/g and M the molar mass of the studied compound. The results are given in Table 2. We compared the calculated enthalpies with respective Zn–N bond lengths and found that higher enthalpy values correspond to Zn–N bond shortening (compare **1** and **2**) and number of nitrogen ligands in the complex (compare **1** and **3**). The enthalpy measured for **1** is suprisingly low but this is in agreement with our observations, which are the following:

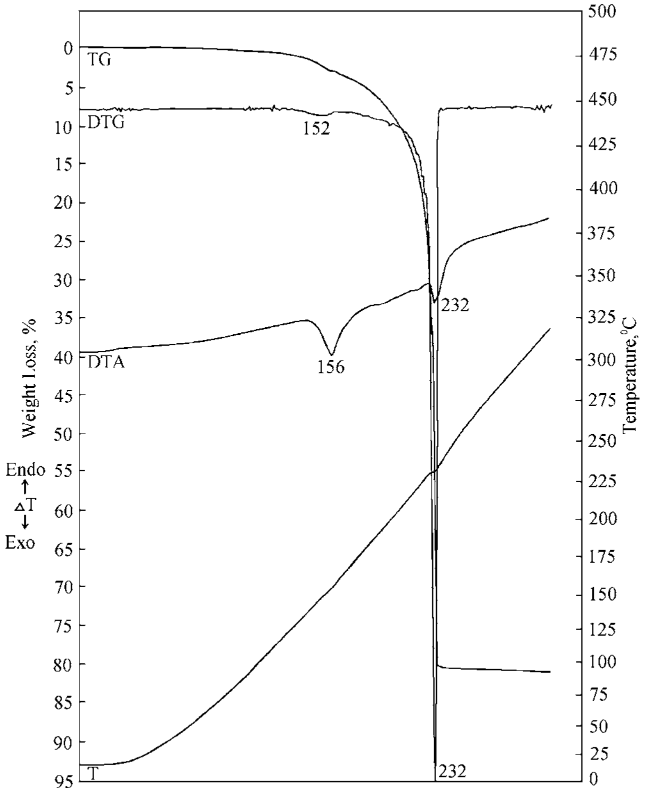


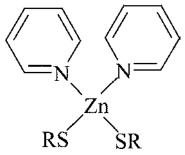
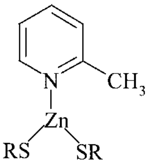
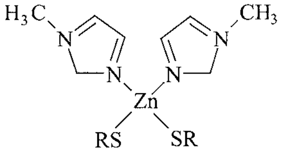
Fig. 8. TG, DTG and DTA curves for bis(tri-*tert*-butoxysilanethiolato) (2-methylpyridine) zinc(II) (**3**) measured in the static air atmosphere.

- $Zn(RS)_2py_2$ losts pyridine much easier than $Zn(RS)_2$ $meim_2$ imidazole. We tried to obtain $Zn(RS)_2meim$ in the same way $Zn(RS)_2py$ was obtained but after prolonged heating we were only partly successful (low yield).
- Even at room temperature the dissociation of $Zn(RS)_2py_2$ slowly proceeds, as smell of pyridine accompanies crystals of $Zn(RS)_2py_2$.
- In the case of sterically hindered derivatives of pyridine (2-picoline, 2,4-lutidine), we were not able to obtain bicomplexes (i.e., introduce two molecules of pyridine on zinc), even when pyridine derivative was used in significant excess.

3.3. *Synthesis of bis(tri-tert-butoxysilanethiolato)-bis(pyridine) zinc(II) (**4**): crystal and molecular structure description*

The synthesis of complex **4** may be the final proof that the decomposition of **1** starts with the partial elimination of pyridine. Complex **4** was synthesized from **1** by simple heating **1** in a drier at 100 °C. As found from the TG curves at this temperature the process of decomposition merely begins so, in our opinion, we did not risk anything but pyridine elimination. We stopped heating when mass loss was equal to the loss of one pyridine moiety per one molecule of complex i.e., 10%.

Table 2
Enthalpies of first stage of decomposition of complexes **1**, **2**, **3** compared to their Zn—N bond lengths

Identification code	Formula[a]	ΔH_1 (kJ/mol)[b]	Length of Zn—N bond (Å) ([8])[c]
1		8 ± 3.4	2.091(5)
3		45 ± 4.9	2.088(4)
2		70 ± 6.2	2.036(5)

[a] *R*: tri-*tert*-butoxysilyl group.
[b] Enthalpy of first stage of thermal decomposition of given compound.
[c] In case of **1** and **2** average length of both Zn—N bonds.

Obtained residue was recrystallized from acetonitrile and the molecular structure of obtained crystals was determined.

The structure of complex **4** with atom labeling schemes showing 30% thermal ellipsoids is illustrated in Fig. 9. Selected bond lengths and angles are gathered in Table 3. Structure of the complex is deposited in Cambridge Crystallographic Data File with the number 249086.

The geometry around zinc atom in complex **4** (Fig. 9) can be described as distorted trigonal bipyramidal with basal plane S(1)–S(2)–N(1), where S(1)–Zn(1)–S(2), S(1)–Zn(1)–N(1) and S(2)–Zn(1)–N(1) angles deviate from the ideal value of 120° but their sum is exactly 360°. O(1) and O(4) atoms occupy two apical positions. The distances between O(1) and O(4) atoms and plane S(1)–S(2)–N(1) are 2.3707(20) Å for O(1) and 2.3864(20) Å for O(4). The deviation of Zn(1) atom from the plane is 0.0281(9) Å (at the O(4) side). Angle O(1)–Zn(1)–O(4) is 178.25°. Both distances Zn–O, which are 2.468 Å (Zn(1)–O(1)) and 2.446 Å (Zn(1)–O(4)), exceed the sum of covalent radii of zinc and oxygen atoms equal to 1.91 Å. Anyway we strongly suggest an interaction between Zn and O(1), O(4) atoms and all the arguments in favour of such suggestion the reader may find in our previous papers [8] as well as in this paper, in

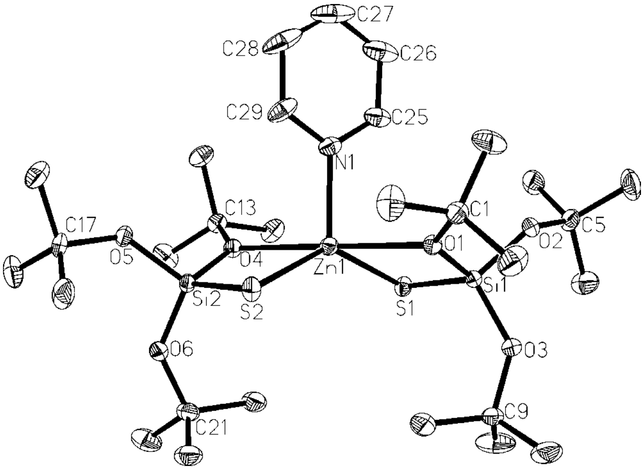


Fig. 9. Molecular structure of bis(tri-*tert*-butoxysilanethiolato)(pyridine) zinc(II) (**4**). All hydrogen atoms are omitted. Only more occupied part of the disordered t-butyl group is shown for clarity.

Table 3
Selected bond lengths [Å] and angles [°] for **4**

Zn(1)—N(1)	2.057(2)
Zn(1)—S(2)	2.2580(8)
Zn(1)—S(1)	2.2666(7)
Zn(1)—O(4)	2.4456(19)
Zn(1)—O(1)	2.4685(19)
S(1)—Si(1)	2.0859(10)
Si(1)—O(3)	1.620(2)
Si(1)—O(2)	1.624(2)
Si(1)—O(1)	1.655(2)
S(2)—Si(2)	2.0823(10)
Si(2)—O(5)	1.621(2)
Si(2)—O(6)	1.625(2)
Si(2)—O(4)	1.655(2)
N(1)—Zn(1)—S(2)	113.30(8)
N(1)—Zn(1)—S(1)	111.00(8)
S(2)—Zn(1)—S(1)	135.65(3)
N(1)—Zn(1)—O(4)	90.82(8)
S(2)—Zn(1)—O(4)	76.61(5)
S(1)—Zn(1)—O(4)	104.99(5)
N(1)—Zn(1)—O(1)	89.55(8)
S(2)—Zn(1)—O(1)	101.68(5)
S(1)—Zn(1)—O(1)	76.45(5)
O(4)—Zn(1)—O(1)	178.25(6)
Si(1)—S(1)—Zn(1)	88.23(3)
Si(2)—S(2)—Zn(1)	88.15(3)

which we observed probable ZnO or $ZnSiO_4$ formation from complex **1**.

We have already described similar complexes of zinc i.e., bis(tri-*tert*-butoxysilanethiolato) (acetonitrile) zinc(II) [7], bis(tri-*tert*-butoxysilanethiolato) (*N*-methylimidazole) zinc(II), bis(tri-*tert*-butoxysilanethiolato) (2-methylpyridine) zinc(II) and bis(tri-*tert*-butoxysilanethiolato) (2,4-dimethylpyridine) zinc(II) [8]. In all these complexes, zinc is pentacoordinated with ZnN_2OS_2 complex core. We have also obtained isomorphous complex of cobalt: bis(tri-*tert*-butoxysilanethiolato)(pyridine) cobalt(II) [12]. The synthesis described in this paper just fills the gap in a series of analogous silanethiolate complexes of zinc and cobalt described by us. We hope that this method will let to receive a new series of zinc complexes; we will try to replace the detached ligands with the new ones.

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References

[1] D.S. Auld, Biometals 14 (2001) 271.
[2] G. Parkin, Chem. Commun. (2000) 1971.
[3] J. Seebacher, M. Ji, H. Vahrenkamp, Eur. J. Inorg. Chem. 2 (2004) 409.
[4] L.M. Berreau, M.M. Makowska-Grzyska, A.M. Arif, Inorg. Chem. 40 (2001) 2212.
[5] S.J. Chiou, C.G. Riordan, A.L. Rheingold, Proc. Natl. Acad. Sci. USA 100 (7) (2003) 3695.
[6] M.A. Ali, A.H. Mirza, C.W. Voo, A.L. Tan, P.V. Bernhardt, Polyhedron 22 (2003) 3433.
[7] B. Becker, K. Radacki, W. Wojnowski, J. Organomet. Chem. 521 (1996) 39.
[8] A. Dołęga, B. Becker, J. Chojnacki, A. Konitz, W. Wojnowski, Inorg. Chim. Acta 357 (2004) 461.
[9] B. Becker, A. Dołęga, A. Konitz, L. Swinder, W. Wojnowski, Z. Anorg. Allg. Chem. 627 (2001) 280.
[10] B. Becker, A. Dołęga, A. Konitz, W. Wojnowski, Polyhedron 20 (2001) 949.
[11] B. Becker, A. Pladzyk, A. Konitz, W. Wojnowski, Appl. Organometal. Chem. 16 (2002) 517.
[12] B. Becker, A. Zalewska, A. Konitz, W. Wojnowski, Polyhedron 20 (2001) 2567.
[13] M. Bochmann, G.C. Bwembya, R. Grinter, A.K. Powell, K.J. Webb, Inorg. Chem. 33 (1994) 2290.
[14] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
[15] G.M. Sheldrick, SHELXL-97, Program for the Solution and the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.
[16] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971, p. 95.
[17] R.C. Weast, M.J. Astle, W.H. Beyer (Eds.), CRC Handbook of Chemistry and Physics, 67th ed., CRC Press Inc., Boca Raton, FL, 1986/1987.